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TEMPORAL VARIABILITY OF AGRICULTURAL CHEMICALS IN GROUND WATER AND IMPLICATIONS FOR WATER-QUALITY SAMPLING

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ABSTRACT

Ground-water monitoring in an extensive citrus region of central Florida has yielded detections of 12 pesticide compounds and elevated nitrate. The 684-mi^2 study area is underlain by relatively homogeneous sandy soils and marine sands that are vulnerable to leaching of agricultural chemicals. Significant temporal variability has been observed in the occurrence of these agricultural chemicals in ground water. Long-term and short-term (quarterly) records of selected analytes between 1993 and 2004 are presented as examples of temporal variations occurring in this ground-water system. Long-term records (12 years) of bromacil and norflurazon in ground water indicated relatively rapid changes corresponding to changes in usage of these pesticides. Quarterly samples from the monitoring wells showed significant temporal fluctuations in concentrations of nitrate (as N), simazine and its degradate (chloroethylamino s-triazine), norflurazon, and aldicarb and its degradates (aldicarb sulfoxide and sulfone), often varying by 100 to more than 200 percent between successive quarters, and at times fluctuating above and below human-health criteria. Dynamic changes in solute concentrations in this region are likely influenced by seasonal rainfall, episodic recharge, minimal organic content of soils (limited sorption of pesticides), and high hydraulic conductivity of soils and subsurface lithologic units, in combination with spatially and temporally episodic chemical-usage patterns. Results of this study indicate that low-frequency sampling (e.g. semi-annual or greater) could underestimate the range and variance of solute concentrations and provide limited definition of agricultural chemical concentrations in ground-water systems.

INTRODUCTION

Monitoring programs designed to assess regional-scale ground-water quality often rely on sampling intervals ranging from annual to multi-year frequency (Gilliom and others, 1995; Barbash and Resek, 1996; Ouellette and others, 1998). Short-term variations of dissolved contaminants in ground-water systems are often assumed to be minimal, on the basis of typically low variability in naturally occurring inorganic constituents, and the generally slow rates of ground-water movement through the subsurface. Additionally, the costly analysis of organic chemicals (e.g. pesticides) often further restricts sampling frequency. However, inferences regarding the magnitude of chemical concentrations with respect to health standards may be misleading in the absence of information on potential variability in concentrations. Furthermore, few ground-water quality networks have been collecting data using consistent design and analytical methods for a sufficiently long period to examine long-term trends in water quality (Barbash and Resek, 1996). Repeat sampling can provide valuable information regarding the effects of changing hydrogeologic influences (such as climate) and land-management practices on ground-water quality.

Water-quality data collected quarterly in a region of concentrated citrus groves in central Florida indicate variations of agricultural chemicals in ground water can be significant, and that long-term changes in chemical concentrations can be related to chemical-usage practices. The Lake Wales Ridge (subsequently referred to in this paper as “the Ridge”), in central Florida (fig. 1), has been the focus of a number of monitoring efforts because of the occurrence of intensive citrus agriculture on sandy soils

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considered vulnerable to leaching of applied chemicals. Seasonally high precipitation rates further enhance the probability of leaching in this area. Based on previous studies on the Ridge indicating transport of agricultural chemicals into the surficial aquifer (Miller and others, 1989; Katz, 1993; Ouellette and others, 1998), a regional monitoring network was established on the Ridge through a cooperative effort between the Florida Department of Agriculture and Consumer Services (FDACS), the U.S. Geological Survey (USGS), and the Southwest Florida Water Management District (SWFWMD) (Choquette and Sepulveda, 2000). The Ridge network consists of 31 wells that are surrounded by citrus groves and which tap the unconfined surficial aquifer. Of the 29 target pesticides and degradates analyzed in samples collected from this network between 1999 and 2004, 12 have exceeded FDACS laboratory detection limits, and include (in decreasing frequency of occurrence): norflurazon, desmethyl norflurazon, simazine, bromacil, diuron, chloroethylamino s-triazine (CEAT), aldicarb sulfoxide, aldicarb sulfone, metalaxyl, aldicarb, imidacloprid, and thiazopyr monoacid (Choquette and others, 2003; web site: http://fisc.er.usgs.gov/Lake_Wales_Ridge/index.html). Detections of target pesticides and degradates in a single well during this period ranged up to as many as eight different compounds; in 55 percent of the wells, five or more different compounds have been detected. Concentrations in a relatively small percentage of samples (<5%) have exceeded drinking-water criteria[1] for five target analytes and two parent-degradate sums. However, concentrations of the pesticides in the Ridge ground water are elevated in comparison to ground-water concentrations in other regions of the United States (Choquette and others, 2003; USGS, 2004). Nitrate concentrations also are elevated in this area, where 90% of the network wells have yielded one or more samples with concentrations exceeding the U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) of 10 mg/L. Long- and short-term records for selected agricultural chemicals are presented as examples to illustrate temporal variations that have occurred in this relatively homogeneous sand aquifer system influenced dominantly by citrus land use. Analytes selected to illustrate long-term changes include bromacil and norflurazon. Analytes selected to illustrate short-term variability include nitrate (as N), norflurazon, simazine and its degradate, and aldicarb and its degradates.

[1]Drinking-water criteria used for reference in this paper include the USEPA MCL's [simazine (4 µg/L); and the sum of aldicarb and its degradates (7 µg/L)]; for compounds with no specified USEPA MCL's, the FDEP health-guidance concentrations (non-enforceable guidelines) were used [norflurazon (280 µg/L), bromacil (90 µg/L), the sum of simazine and its degradates (4 µg/L)].

DESCRIPTION OF THE STUDY AREA

The study area (fig. 1) is defined by the Lake Wales Ridge physiographic feature (Brooks, 1981) within Polk and Highlands Counties and covers an area of 684 mi^2. Polk and Highlands Counties were the top two counties statewide for 2002-2003 total annual citrus production (National Agricultural Statistics Service web page data, http://www.nass.usda.gov/fl/rtoc0ci.htm), and represent one of the most productive citrus regions in the world. Citrus groves cover 169 mi^2 (24 percent) of the study area (Southwest Florida Water Management District, 1998).

The subsurface of the Ridge consists of a mantled karst terrain where unconsolidated Pliocene-Pleistocene relict beach and dune deposits overlie an irregular limestone surface (Brooks, 1981). The surficial aquifer predominantly consists of fine to coarse sand that thickens from about 50 ft in the northern part of the study area to more than 300 ft in the south (Barcelo and others, 1990; Yobbi, 1996). The soils in this region typically consist of fine to medium sand, contain less than 1 percent organic carbon, and less than ½ to 2 percent organic matter in the surface layer (U.S. Department of Agriculture, 1989 and 1990). Sand-sized particles comprise about 97 to 99 percent of these soils and hydraulic conductivity is high, typically 24 to 51 in/hr throughout the soil profile. Mean annual rainfall in the vicinity of the Ridge ranges from about 45 to 51 inches, with about two-thirds occurring during summer months (National Oceanic and Atmospheric Administration (NOAA), 2003). Precipitation rates, particularly from convective and tropical storms, can be quite high.

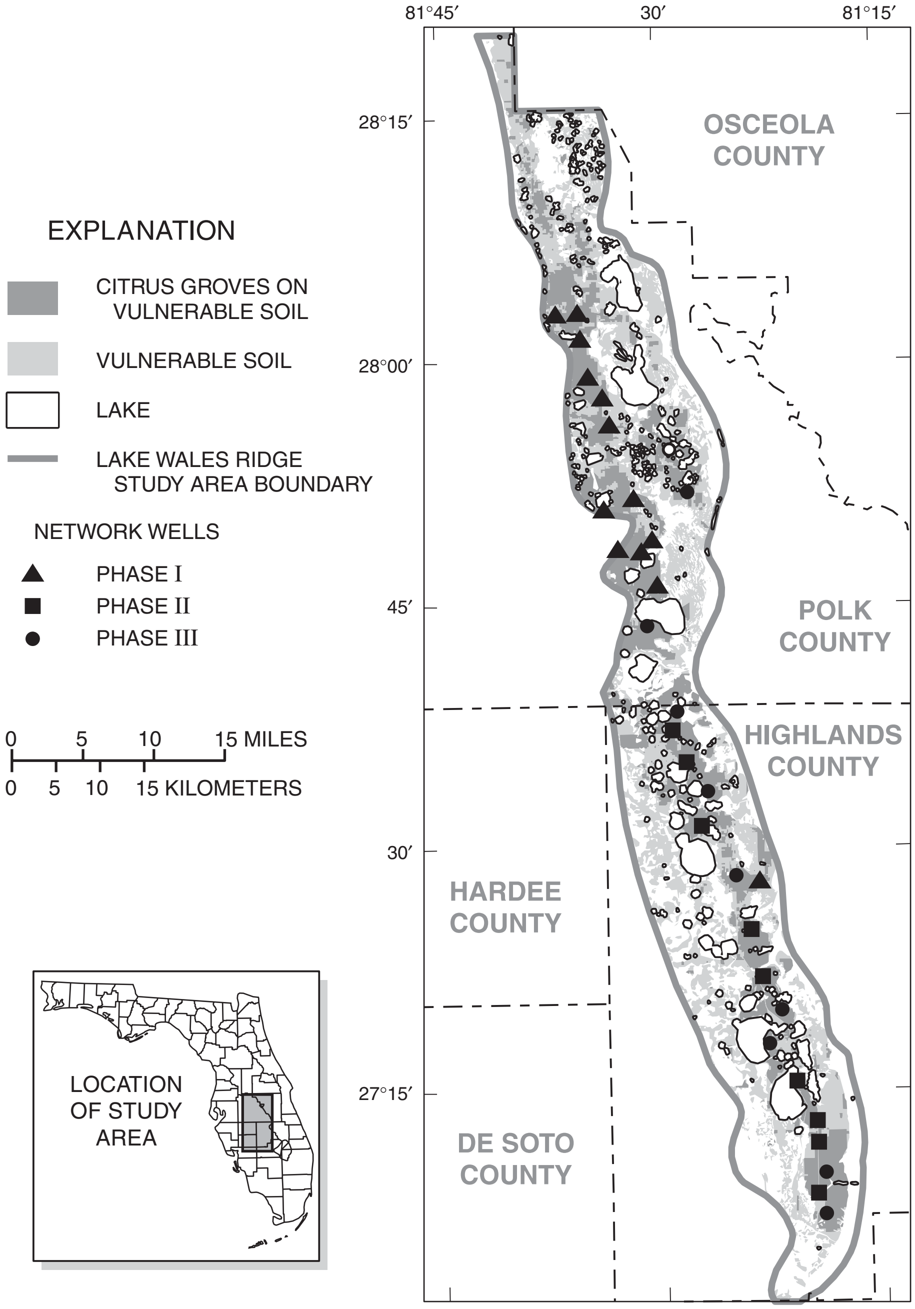

Figure 1. Extent of citrus land use and vulnerable soils in the study area, and locations of network wells. Vulnerable soils are defined as sandy, well-drained soils prone to leaching (State of Florida, 1994).

Traveltimes for ground water to move through the unsaturated zone to the water table vary locally due to a number of factors including climate conditions, soil moisture and morphology, and lithology and thickness of the unsaturated zone. Local-scale studies on the Ridge using conservative tracers indicate that transport rates can vary significantly over time and space; where the depth to water table ranged from about 9 to 15 ft, traveltimes ranged from about 2 to 10 months (Graham and Alva, 1997; Danny Moore, Florida Dept. of Agriculture and Consumer Services, written commun., June 5, 2003). Preferred pathways of flow, commonly referred to as "flow fingering," can contribute to variations in traveltimes through the unsaturated zone (Glass and others, 1988). Small-scale heterogeneities in the Ridge sands contribute to the development of flow fingers in the study area (Pendexter and Furbish, 1991), which may decrease ground-water traveltimes by a factor of 2-3 times faster than expected from a uniform wetting front. Previous studies of the surficial aquifer in the vicinity of Polk and Highlands Counties indicate an average specific yield ranging from about 25 to 30 percent, and a range in hydraulic conductivity from about 0.9 to 24 ft/day (Barr, 1992; Yobbi, 1996; Graham and Alva, 1997).

SAMPLING NETWORK AND LABORATORY ANALYSES

The Ridge monitoring network was established in three phases and currently includes quarterly sampling of 31 wells (fig. 1). Well sites were randomly selected using grid sampling within the areas of citrus groves on soils classified as vulnerable to leaching, which include about 93 percent of the citrus area on the Ridge (Choquette and Sepulveda, 2000). The network is envisioned to be a long-term monitoring effort (10 to 20 years) that will provide early warning of agricultural chemical transport into the surficial aquifer, assess spatial and temporal variability of agricultural chemicals in ground water, and identify potential factors affecting the occurrence of agricultural chemicals in the aquifer. Phase I sampling (12 wells), Phase II sampling (9 wells), and Phase III (10 wells) began in April 1999, April 2000, and October 2001, respectively. Phase I consisted of existing monitoring wells, and Phases II and III consisted of new wells. Eleven of the Phase I wells had been sampled intermittently between 1989 and 1999 by the Florida Department of Environmental Protection (FDEP), the SWFWMD, and the USGS. Well depths range from about 21 to 150 ft below land surface, and depth to the water table ranges from about 4 to 103 ft below land surface.

Water samples were collected and processed using Teflon or stainless steel equipment according to FDEP ground-water sampling protocols (Florida Dept. of Environmental Protection, 2002; Morse, 1999), which included a minimum purge of three well volumes and stabilization of pH, dissolved oxygen, specific conductance, and temperature. Samples were analyzed for major dissolved inorganic constituents, nutrients, pesticides, and selected trace constituents. Nitrate (as N, throughout this paper) and pesticide analyses were performed at the FDACS Pesticide Laboratory and included USEPA and FDACS custom methods (Rygiel, 2001 and 2003; Brock and Rygiel, 2003; Page and Stepp, 2003).

RESULTS AND CONCLUSIONS

Data collected for this monitoring program indicate temporal changes in long-term detection of pesticides as well as significant short-term fluctuations in concentrations of nitrate and pesticides. Long-term sampling records available for a subset of the Phase I network wells (fig. 2) show changes in

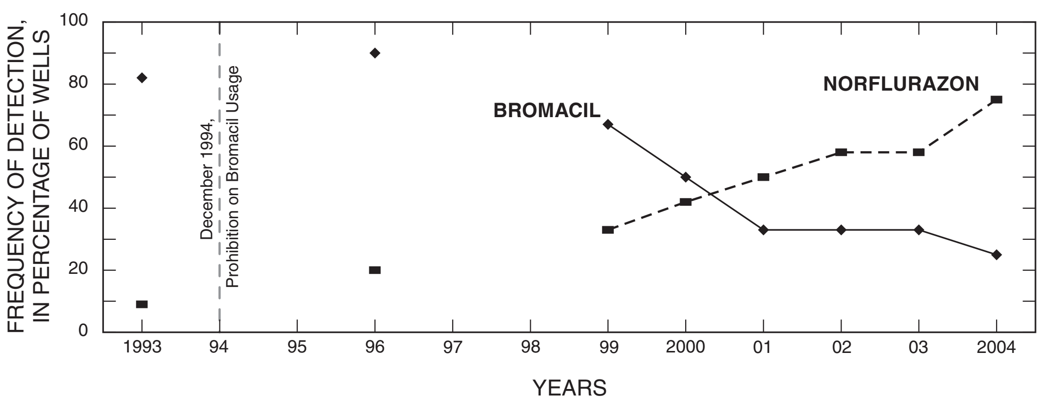

Figure 2. Detections of bromacil and norflurazon at a subset of network wells (n=11) with long-term records. In December 1994, bromacil use was prohibited from use in citrus groves on well-drained sandy soils vulnerable to leaching. Laboratory detection limits were 2 µg/L for bromacil and 1 µg/L for norflurazon.

ground-water quality that correspond with changes in pesticide-usage practices. Bromacil detections occurred in 82 percent of the wells in 1993, 90 percent in 1996, and subsequently declined from 68 percent to 25 percent between 1999 and 2004 (fig. 2). During this period, norflurazon detections steadily increased from 10 to 75 percent. Bromacil was prohibited from use in most Ridge citrus areas in December 1994 (State of Florida, 1994), and was subsequently replaced by other herbicides including norflurazon and glyphosate. The continued pervasive occurrence of bromacil in ground water about 1.5 years after the ban on its usage is likely due to the chemical persistence of bromacil as well as the time required for the chemical to travel into and through the ground-water system. Measurements of the half life of bromacil range from 2 to 8 months in soils and up to 2 months in water (Hornsby and others, 1996; Spectrum Laboratories Chemical Fact Sheet, http://www.speclab.com/compound/c314409.htm). Chemical persistence in source areas is indicated by the continued bromacil detections at 25 percent of these wells in 2004, nearly 10 years after its ban. Although it is difficult to verify that bromacil has not been applied in the regions surrounding these wells during the 1995 to 2004 period, its estimated use was likely negligible based on the sparsity of non-citrus areas in the vicinity of wells and the fact that it has not been used in this area for roadside weed control (Danny Moore, FDACS, pers. comm., July 2003).

Increasing detections of norflurazon in ground water in these Phase I wells coincides with increasing trends in measured concentrations at a number of network wells (fig. 3). In these wells, the highest concentrations and fluctuations occurred where the water-table depths were relatively shallow (averaging 23 ft below land surface), and where sampled zones (well screens) were both short (10-11 ft) and in close proximity to the water table (wells 1 through 3, fig. 3). Lower and less variable concentrations occurred in wells 4 through 8 (fig. 3) where water-table depths were generally deeper (averaging 41 ft below land surface), and sampled zones were longer (20 ft) and(or) deeper within the saturated zone (as much as 47 ft). The FDEP health-guidance level (280 µg/L) for norflurazon has not been exceeded in samples collected from network wells through 2004.

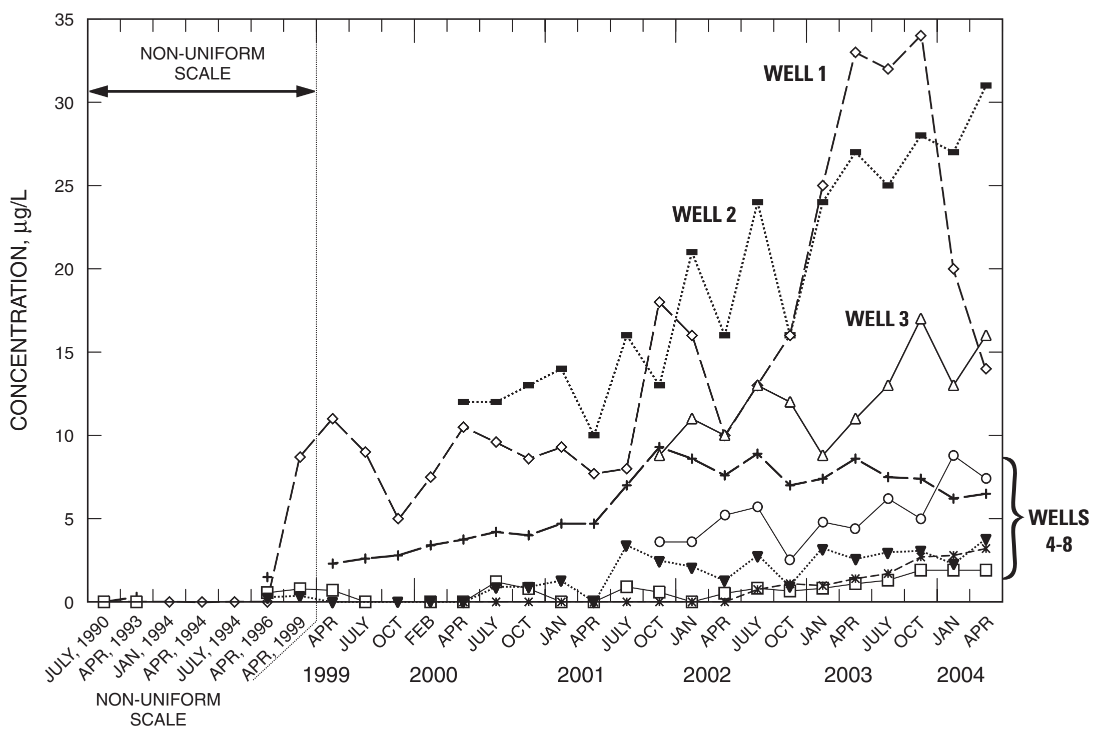

Figure 3. Trends in concentrations of norflurazon in ground water from selected Ridge network wells. Concentrations have not exceeded the Florida health-guidance value for norflurazon (280 µg/L).

In ground water from network wells, temporal variations in concentrations of most detected pesticide compounds and nitrate were significant, often varying by 100 to 200 percent between quarters. In figure 4, results are shown for wells that yielded some of the highest concentrations of simazine and its degradate chloroethylamino s-triazine (CEAT[2]); aldicarb and its degradates aldicarb sulfone and sulfoxide; and nitrate. Concentrations of these compounds in ground water from some wells fluctuated above and below human-health criteria between consecutive quarters.

The water-table depths and sampling (well-screen) depths at these wells (fig. 4) also indicate that there may be some association between the magnitude and variability of agricultural chemical concentrations and the depth zone of ground water sampled. The simazine-degradate and aldicarb-degradate concentrations were generally highest and most variable at sites with shallow water tables (averaging 30 and 39 ft in figs. 4 a and b, respectively) and from shorter sampled zones (10-ft-long screened intervals) near the water-table interface (fig. 4 a and b). Elevated nitrate concentrations, however, extended to deeper water-table depths (averaging 57 ft in fig. 4c) and deeper within the saturated zone of the aquifer: occurring at water-table depths of 97 to 103 ft below land surface, and from 20-ft-long screened (sample) intervals at depths as much as 22 to 53 ft below the water table (fig. 4c). These data indicate a need for additional evaluation of vertical and areal patterns in agricultural chemical concentrations including all network wells to determine if patterns are consistent and if causative factors can be related to observed patterns. Such spatial variability in chemical concentrations could be related to usage history and properties of the chemicals (e.g. persistence, solubility, sorption potential), as well as a number of other biogeochemical factors, such as redox conditions, pH, microbial populations, and ground-water ages. Analysis of the influence of these factors on water quality of ground water and lakes on the Ridge is ongoing (web site: http://fisc.er.usgs.gov/Lake_Wales_Ridge/index.html).

Results from the Ridge network indicate the presence of complex spatial and temporal distributions of agricultural chemicals in the unconfined, surficial aquifer system, in spite of the generally uniform crop type in the vicinity of wells, and the relatively homogenous soils and lithology on the Ridge. The dynamic variability of agricultural chemicals in ground water in this region is likely due to a number of factors including the episodic nature of chemical applications and of ground-water recharge, combined with variations of agricultural chemical properties and relatively rapid recharge rates and transport via preferential pathways (flow fingering) within the unsaturated zone (Pendexter and Furbish, 1991). The water-quality data indicate that the variance of solute concentrations would likely be underestimated with longer sampling intervals. These results underscore the need for evaluations of agricultural chemicals in ground water to include assessment of short-term temporal variability in order to accurately depict water-quality conditions and human-health risks associated with drinking-water sources.

[2] CEAT is equivalent to desmethyl simazine and deisopropylatrazine.

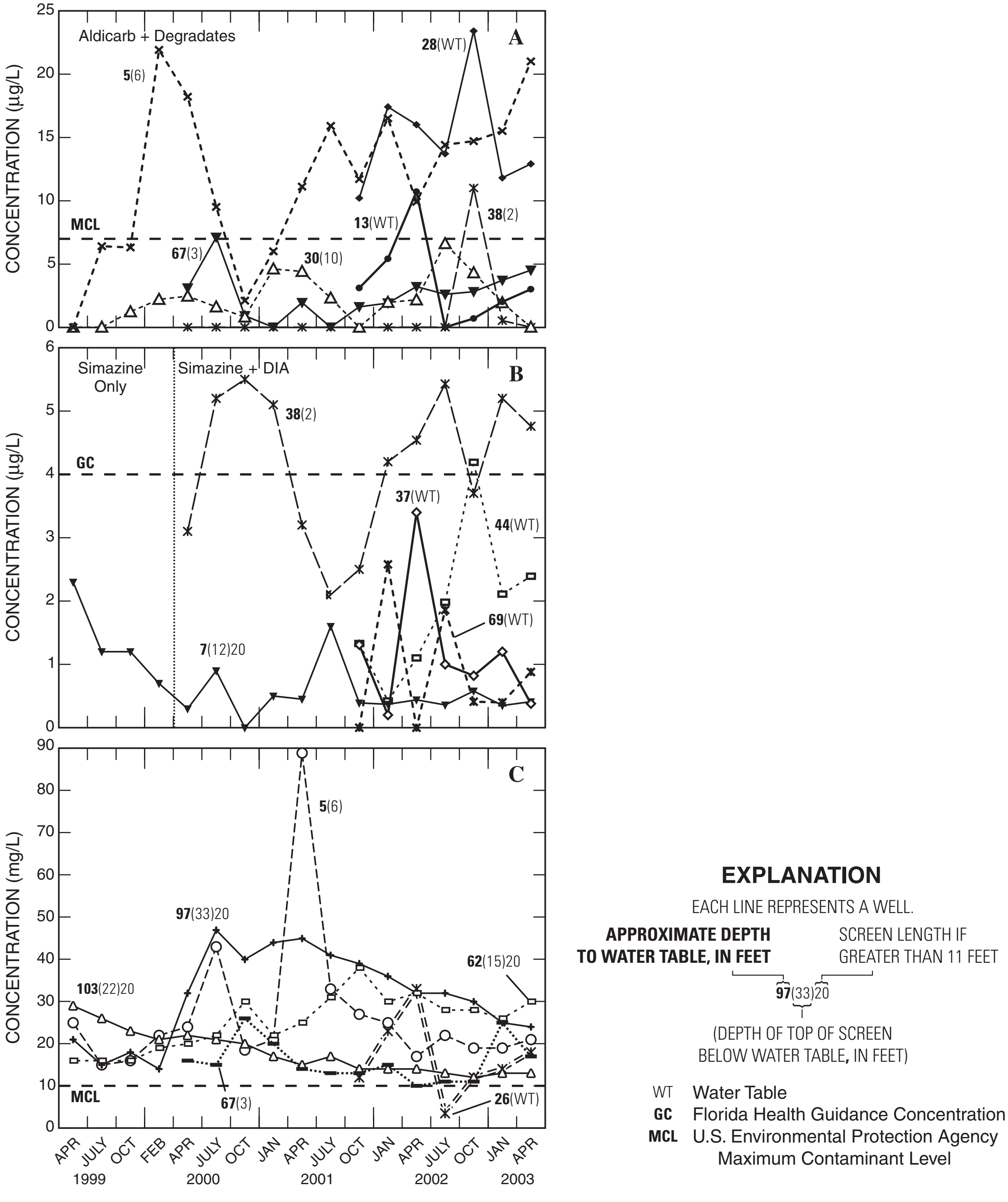

Figure 4. Concentrations of (A) aldicarb and its degradates: aldicarb sulfone and sulfoxide; (B) simazine and its degradate, chloroethylamino s-triazine (CEAT); and (C) nitrate, as N, in ground water from selected wells.

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